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Properties of refined milkweed press oil

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Abstract

The seed floss from *Asclepias* is currently harvested as a hypoallergenic fiber fill material for use in pillows and comforters. Milkweed seed is harvested with the floss although the oil contained in the seed is not used commercially. Milkweed oil was investigated as an alternative source of triglycerides for potential industrial applications. Processing conditions were investigated to produce degummed, refined, and bleached press oil. Milkweed oil was expelled from whole seed using a pilot-scale press and processed in the laboratory to produce refined and bleached oil. A high quality oil with a Lovibond color of 2Y and 0.2R was obtained following degumming with 3 wt.% water, refining with 3 M sodium hydroxide, and bleaching with 5% activated earth.
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1. Introduction

The seedpods of two wild-type milkweed species, *Asclepias syriaca* and *A. speciosa*, are harvested for seed floss in the North Central United States (Witt and Nelson, 1992; Von-Bargen et al., 1994; Zeller and Knudsen, 1996). Milkweed seed floss has a high thermal insulating property and has been evaluated for use in woven and non-woven textile applications (Louis and Andrews, 1987; Crews et al., 1991). The seed floss is used commercially as a hypoallergenic fiber fill material (Natural Fiber Corp., Ogallala, NE).

In the current application of milkweed seed floss, the seed is a by-product with value as a naturalizing plant for highway beautification, landscaping, and erosion control. However, the markets for these applications are limited. The seed contains approximately 23 wt.% triglycerides with a C18 fatty acid composition of 50% linoleic, 34% oleic, and 1% linolenic. Recovery of this oil and identification of marketable applications would provide alternative uses for the seed and enhance the economic value of milkweed. Additionally, the defatted milkweed seedmeal has demonstrated nematicidal activity in greenhouse and field tests when used as a soil amendment (Harry-O'Kuru et al., 1999).

This laboratory study investigated conditions required to degum, refine, and bleach milkweed

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pressed oil. Identification of appropriate processing conditions for milkweed press oil is an initial step toward the introduction of the oil as an alternative triglyceride source.

2. Experimental

2.1. Materials

Milkweed seeds from *A. syriaca* and *A. speciosa* were provided by the Natural Fiber Corp. (Ogallala, NE). These seeds were harvested during the 1997 season and separated from the seed floss. Sodium hydroxide solutions were prepared with de-ionized water and standardized prior to use (Fisher Scientific International, Inc., Hampton, NH). Celite was used as a filter aid for the filtration of oil samples (J.T. Baker, Inc., Phillipsburg, NJ). Four bleaching earths were tested including, the American Oil Chemists Society (AOCS) Activated Bleaching Earth (AOCS, Champaign, IL), Filtrol Nevergreen (Engelhard Corp., Edison, NJ), Tonsil L-80 (L.A. Salomon Inc., Port Washington, NY), and AOCS Natural Bleaching Earth (AOCS, Champaign, IL).

2.2. Methods

Milkweed oil was obtained by pressing whole milkweed seeds with a pilot-scale expeller (serial number 2245, Hander Oil Machinery Corp., Osaka, Japan) at Iowa State University, Ames, Iowa. A total of 120 kg of milkweed seed was pressed at a feed rate of 40 kg/h. The choke was adjusted during the operation of the press to minimize the generation of particulates. The press barrel temperature was maintained between 80 and 90 °C.

The defatted meal generated from the first press operation was collected and also pressed. These first and second press oils were collected separately and filtered. These filtered crude oils were subsequently centrifuged (Model AS-16P Super Centrifuge, The Sharples Corp., Philadelphia, PA) to remove components that settled during storage and then stored at −5 ° C under nitrogen.

Samples of the press oils were degummed in 100 g batches with the addition of deionized water at 1, 3, or 5 wt.%. Degumming was performed at 25 or 50 °C on a programmable hot plate stirrer equipped with temperature control (Cole-Parmer Instrument Co., Chicago, IL). The oil/water mixture was held at the designated temperature for 20 min. Precipitates were removed by centrifuging for 10 min at $2100 \times g$ (Model Centra-CL2, International Equipment Company, Needham Heights, MA).

Degummed milkweed oil was refined with the addition of either 2 or 3 M sodium hydroxide at 0.1% excess. This amount was calculated to provide sufficient base to neutralize the free fatty acids (FFA) without hydrolyzing additional triglycerides. The oil was refined at 30 °C with agitation and the appropriate amount of sodium hydroxide solution added. After 15 min at 30 °C, the temperature was raised to 50 °C to break the emulsion and allowed to cool. The mixture was centrifuged for 15 min at $2100 \times g$ and the refined oil stored under nitrogen at −5 °C.

Refined and degummed milkweed oil was bleached under vacuum, 60 mm Hg, in a laboratory rotary evaporator (Model RE-121, Buchi Labortechnik AG, Flawil, Switzerland) equipped with a heating bath. Oil samples were combined with 5 wt.% bleaching earth. AOCS Activated Bleaching Earth, AOCS Natural Bleaching Earth, Filtrol Nevergreen, and Tonsil L-80 were tested. The mixture of oil and bleaching earth was maintained at 50, 70, or 90 °C and a rotor speed of 150 rpm. After a 20 min contact time, the oil was separated from the bleaching material by vacuum filtration.

2.3. Analytical

Fatty acid compositions were determined by gas–liquid chromatography after conversion to the corresponding methyl esters by AOCS Official Method Ce 1-62 (AOCS, 1994). Analyses were performed on a Hewlett-Packard 5890 gas chromatograph (Palo Alto, CA) equipped with a flame ionization detector. Separations were achieved using an SP-2380 column (Supelco, Bellefonte, PA) of 60 m × 0.25 μm with a film thickness of 0.2

μm. A temperature program was used starting at 100 °C for 5 min, 100–190 °C at 3 °C/min, 190–200 °C at 1 °C/min with a 5 min hold time, and 200–250 °C at 5 °C/min with a 5 min hold time for a total run time of 65 min. The inlet temperature was maintained at 250 °C. Injection volumes of 2 μl were used with a split ratio of 99:1. Helium was used as the carrier gas. Identifications of the resulting fatty acid methyl esters were made by comparison to standards.

Determinations of FFA, phosphorus, and oxidative stability index (OSI) were made by AOCS Official Methods Ca 5a-40, Ca 12b-92, and Cd 12b-92, respectively (AOCS, 1994). Lovibond color value was determined with a Model AF710 Tintometer (The Tintometer, Ltd., Salisbury, UK) according to AOCS test method Cc 13b-45. Seed moisture and oil content were determined by AOCS Official Method Ac 2-41 and Ba 3-38, respectively (AOCS, 1994). Peroxide values were determined by AOCS Official Method Cd 8b-90. All analyses were run in duplicate with a relative standard deviation of less than 5%.

2.4. Statistical analysis

Experimental designs and data analyses were performed with MINITAB version 13.32 (MINITAB, Inc., College Station. PA). A full factorial experimental design was used to investigate the effects of temperature and water on the quality of degummed oil. Two temperature levels and three water levels were tested. The FFA content was chosen as the response variable. A full factorial experimental design was also used to investigate the effects of temperature and bleaching earth on the degummed and refined oil. Three temperature levels and four types of bleaching earths were tested. The experimental designs were randomized and performed in a single block.

3. Results and discussion

3.1. Press oil

Milkweed seeds were determined to contain 8 wt.% moisture and 23 wt.% oil on a dry weight basis (dwb). Crude first and second press oils were collected and evaluated for FFA, phosphorus, Lovibond color, and OSI (Table 1). First press oil produced a yield of 12.1 and the second press produced only 2.5% (dwb). These yields are lower than may be expected from a solvent extraction process. However, solvent extracted oil would not be acceptable in certain cosmetic and personal care formulations and requires more capital equipment to produce. Optimization of the press for milkweed seed could increase the yield of the first press oil. The yield of second press oil was low and would not justify the additional processing time in a large-scale operation. The phosphorus content of these press oils indicates the need for a separate degumming step to reduce the amount of phospholipids. The degumming step will also facilitate the refining process. The oxidative stabilities of both first and second press oils were less than 3 h. For comparison, crude press oils obtained from flaked meadowfoam seeds, *Limnanthes alba*, were determined to have oxidative stability indices (OSI) between 24 and 42 h depending on flake thickness and tempering conditions (Holser and Isbell, 2002). The OSI characterizes the ability of the oil to resist oxidation and is an important parameter in identifying conditions that preserve oil quality.

Table 1
Properties of crude press oils from *A. syriaca* and *A. speciosa* seeds

Press	Yield (%)	*P* (ppm)	Lovibond color		OSI (h)
			Yellow	Red	
First	12.1±0.6	288±14	35±1	7±1	2.72±0.07
Second	2.5±0.1	337±17	70±2	4±1	2.35±0.06

The fatty acid composition of milkweed oil was determined by gas chromatography following trans-esterification of the triglycerides and recovery of the corresponding methyl esters. First press milkweed oil consists of over 90% unsaturated fatty acids with a fatty acid distribution of: 15.1%, 16:0; 5.7%, 16:1; 1.1%, 16:2; 2.6%, 18:0; 14.1%, 18:1 (11); 20.3%, 18:1 (9); 49.6%, 18:2; 1.0%, 18:3; 0.3%, 20:0; and 0.2%, 20:1. The high unsaturated fatty acid content and the correspondingly low OSI values indicate that oxidizing conditions be avoided during processing to produce a high quality oil with minimum refining losses.

3.2. Degumming, refining, and bleaching

The responses of crude milkweed oil to different degumming, refining, and bleaching treatments were evaluated in terms of FFA content, color, phosphorous content, and peroxide value. We examined three water contents for degumming, two caustic contents for refining, and four different types of bleaching earths. Temperatures selected for degumming, refining, and bleaching were lower than normally used for other seed oils due to the low OSI value of crude milkweed oil.

The results of the degumming experiments showed a significant effect of both water content and temperature on phosphorus (Table 2). Degumming with 5% water reduced the phosphorus content from 288 ppm in the crude oil to 47 ppm at 25 °C and 49 ppm at 50 °C. Degumming with 1 or 3% water was less effective in removing phosphorus, e.g. 71 and 62 ppm, respectively, at 50 °C. However, the highest FFA values, 4.8%, were obtained at 50 °C and 5 wt.% water. All other treatments produced oils with FFA values of between 1.1 and 2.3%. Higher temperatures appear to generate larger amounts of FFA that will subsequently require more sodium hydroxide to refine the oil. Therefore, the higher temperature should be avoided during degumming.

Degummed oil samples were refined with either 2 or 3 M NaOH. The amount used was calculated based on the FFA value with a 0.1% excess of that required for neutralization. This value was selected to minimize triglyceride losses due to acid hydrolysis. Oil samples refined with 2 M NaOH were determined to have a mean value ($N = 10$) of

Table 2
Analysis of variance for degumming treatments on phosphorus content

Source	DF	Sum of squares	Adjusted mean squares	F-ratio	P-value
% Water	2	319.74	159.87	8.80	0.010
Temperature	1	300.00	300.00	16.51	0.004
Error	8	145.34	18.17		

Table 3
Analysis of variance for refining treatments

Source	DF	Sum of squares	Adjusted mean squares	F-ratio	P-value
Molarity	1	0.00028	0.00028	0.12	0.732
Error	17	0.03909	0.00230		
Total	18	0.03937			

0.0191 ± 0.0015% FFA and oil samples refined with 3 M NaOH were determined to have a mean value ($N = 9$) of 0.0183 ± 0.0017% FFA. The analysis of variance indicated there was no significant difference between these two treatment levels (Table 3).

Four bleaching earths were tested to determine the most effective treatment for refined milkweed oil. Experiments were conducted at 50, 70, and 90 °C. Three of the four bleaching earths were acid activated bentonite clays. Activation of a bleaching earth provides more surface area for the adsorption of impurities and enhance the catalytic properties of the clay. This reduces the amount of material required for the decolorization of oils, however, the increased reactivity of the clay can lead to the formation of undesirable reaction products during the bleaching treatment. To explore this behavior, the effect of temperature and bleaching earth on FFA and peroxide values were tested for significance. Table 4 displays the ANOVA results for FFA. The calculated P-values are greater than 0.05 for both temperature and bleaching earth. The effects are not considered significant at this level. However, when a confidence level of 0.15 was selected then the null hypothesis would be rejected and the effect of temperature on FFA would appear to be significant. It is reasonable to expect higher temperatures to promote the formation of FFA in the presence of an acid catalyst. Conventional bleaching treatments are performed between 80 and 120 °C. Therefore, it is likely that the effect of temperature on FFA would become more pronounced at the higher temperatures. Table 5 displays the ANOVA results for the effect of temperature and bleaching earth on peroxide value. Temperature clearly has a significant effect on the peroxide value. The highest bleaching temperature, 90 °C, resulted in the lowest peroxide values for all the bleaching earths tested (Table 6). This is consistent with the function of the bleaching earth to remove impurities such as primary oxidation products. The lower temperatures were not effective in reducing the peroxide value of the oil. The peroxide value increased at 70° in the presence of Tonsil and AOCS Natural bleaching earths. This is probably due to competing rates of formation of oil oxidation products and removal by the bleaching earths. These treatments also generated an increase in

Table 4
Analysis of variance for bleaching treatments on FFA

Source	DF	Sum of squares	Adjusted mean squares	F-ratio	P-value
Earth	3	4.720	1.573	0.89	0.500
Temperature	2	10.320	5.160	2.90	0.131
Error	6	10.661	1.777		
Total	11	25.701			

Table 5
Analysis of variance for bleaching treatments on peroxide value

Source	DF	Sum of squares	Adjusted mean squares	F-ratio	P-value
Earth	3	13.285	4.428	1.52	0.304
Temperature	2	35.921	17.961	6.15	0.035
Error	6	17.533	2.922		
Total	11	66.740			

Table 6
Tintometer color and peroxide values for refined and bleached milkweed oil

Earth	Temperature (°C)	Color[a]		Peroxide value (meq/kg)
		Yellow	Red	
AOCS activated	50	6	0.7	2.7±0.1.
	70	2	0.3	2.6±0.1
	90	10	2.0	1.2±0.1
Filtrol	50	40	4.0	6.5±0.3
	70	2	0.2	6.4±0.3
	90	3	0.7	1.3±0.1
Tonsil	50	3	0.5	3.6±0.2
	70	50	1.0	6.6±0.3
	90	10	1.2	2.5±0.1
AOCS Natural	50	35	2.0	2.8±0.1
	70	50	1.0	8.8±0.4
	90	6	0.8	2.4±0.1

[a] Mean values with CV = 0.05.

yellow color values that indicate the formation of color bodies. These competing rate processes appear to reverse as the temperature is increased to 90 °C.

The most effective temperature for reducing the yellow color value in refined milkweed oil was 70 °C for both the AOCS Activated and Filtrol Nevergreen earths (Table 6). The AOCS Natural agent was most effective at 90 °C. The most effective temperature for reducing the red color value was 70 °C using AOCS Activated and Filtrol Nevergreen bleaching earths. Higher and lower temperatures were less effective for bleaching the refined milkweed oil. These results indicate that both of these bleaching earths would be effective for decolorization. The choice between these two may depend on the intended application of the oil and a subsequent vacuum deodorization treatment that would remove any remaining oxidation products.

4. Conclusions

Milkweed seed may be expelled to produce a crude oil composed of predominately unsaturated fatty acids. The oil exhibits a very low oxidative stability and precautions are required to preserve the oil quality. The crude milkweed oil was water degummed at 25, caustic refined at 30, and bleached at 70 °C to generate a triglyceride product suitable for industrial applications.

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